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FILM FORMATION IN BINARY SOL-GEL SYSTEMS

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The film-forming capacity of binary systems containing Sb_2O_3, SnO_2, CeO_2, Y_2O_3, Nd_2O_3, Bi_2O_3, V_2O_5, ZnO, CuO, CdO, and Al_2O_3 are investigated. The best film-formers are Sb_2O_3 and SnO_2, whereas ZnO, CuO, CdO, and Al_2O_3 cannot produce films of optical quality. The rest of considered oxides do not impair the clarity of coatings when their molding content is 20 – 50%. A proportional dependence is established between the refractive index and the reflection coefficient of a film and the refractive indexes of oxides making parts of this film, as well as between the concentration of deposited FFS, the film-forming capacity of oxides, and the film thickness.

Modification of sheet glass surface using transparent films makes it possible to obtain new materials with a set of unique properties. The sol-gel technology of depositing coatings from solutions is the most promising and attractive due to the simplicity and low cost of equipment, as well as the simplicity and reliability of the production process. The method is now widely used for the deposition on heat glass to produce current-conducting, heat-reflecting, and decorative coatings containing tin, antimony, indium and titanium oxides. There are obviously numerous oxides promising for application in sol-gel technology, however, the progress in this field is delayed by a lack of data on their form-forming capacity and properties.

The purpose of our study is the investigation of film formation in binary systems.

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The criteria for the choice of components were the refractive index of oxide and good solubility of its chloride in ethanol, which is traditionally used in sol-gel systems.

Film-forming solutions (FFS) were prepared using oxides of a grade not lower than “pure” and rectified ethyl alcohol (ethanol) with the content of the main material not less than 96%.

To prepare a single-component FFS with a required oxide concentration, the required portion of Me_xO_y was dissolved in a precisely calculated quantity of hydrochloric acid of a grade not less than “pure” and diluted with ethanol. Binary solutions were obtained by mixing single-component solutions in required proportions. The FFS were exposed during several days for aging, then deposited by immersion on sheet glass samples and fixed in short-time firing.

The state of the coatings (transparency, continuity, presence of crystals) was estimated visually. Externally trans-

TABLE 1

Cation in Me_xO_y composition	Cation in Me'_aO_b composition										
	V	Sn	Ce	Al	Y	Sb	Nd	Bi	Cu	Zn	Cd
V	–	+	–	+	+	+	–	+	+	+	+
Sn	+	–	+	–	+	+	+	+	+	+	+
Ce	–	+	–	–	+	+	+	+	+	+	–
Al	+	–	–	–	+	–	–	–	–	–	–
Y	+	+	+	+	–	+	+	+	+	+	+
Sb	+	+	+	–	+	–	+	+	+	+	+
Nd	–	+	+	–	+	+	–	+	+	+	+
Bi	+	+	+	–	+	+	+	–	+	+	–
Cu	+	+	+	–	+	+	+	+	–	+	+
Zn	+	+	+	–	+	+	+	+	+	–	+
Cd	+	+	–	–	+	+	+	+	+	+	–
Considered compositions/systems	42/8	54/9	37/7	10/2	48/10	37/37	30/8	39/9	39/9	50/9	24/7

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parent films or films with slight turbidity were subjected to the analysis of their physical properties: refractive index, reflection coefficient, and thickness. The refractive index and thickness were determined ellipsometrically and the reflection coefficient was measured with a Pulsar spectrocolorimeter.

Table 1 lists investigated oxides (the investigated binary systems $Me_xO_y - Me'_aO_b$ are designated by the sign "+"). Each system, depending on its expected film-forming system capacity, was used to prepare from 1 to 6 FFS compositions, which differed in the total weight content of film-forming oxides (2.5 and(or) 5%) and the molar ratio of these oxides (20 Me_xO_y, 80 Me'_aO_b; 50 Me_xO_y, 50 Me'_aO_b; 80 Me_xO_y, 20 Me'_aO_b).

Film-coated samples were divided into 4 categories based on their exterior appearance: transparent (T), continuous opaque (OC; this category includes coatings with different degrees of turbidity uniformly spreading over the base), opaque discontinuous (ODC; films with poor adhesion to glass substrate and, consequently, nonuniform spreading); and films with intense crystallization (Cr). Table 2 shows the distribution of samples with coatings classified among the above categories.

The analysis of data in Table 2 shows that the systems are ranked in the following series in the descending order of measured properties (numbers below the oxide formula indicate the relative number of films with the specified property):

$$\text{T: } \underset{73.0}{Sb_2O_3} \rightarrow \underset{59.0}{SnO_2} \rightarrow \underset{22.0}{CeO_2} \approx \underset{21.0}{Y_2O_3} \approx \underset{27.0}{Nd_2O_3} \approx \underset{25.6}{Bi_2O_3} \rightarrow \underset{17.0}{V_2O_5} \rightarrow \underset{4.0}{ZnO} \approx \underset{2.6}{CuO} \approx \underset{0}{CdO} \approx \underset{0}{Al_2O_3};$$

$$\text{OC: } \underset{50.0}{ZnO} \approx \underset{47.5}{V_2O_5} \rightarrow \underset{42.0}{CdO} \rightarrow \underset{26.0}{Bi_2O_3} \approx \underset{22.0}{Sb_2O_3} \approx \underset{22.0}{SnO_2} \approx \underset{18.0}{CuO} \rightarrow \underset{12.5}{Y_2O_3} \rightarrow \underset{0}{Al_2O_3} \approx \underset{0}{CeO_2} \approx \underset{0}{Nd_2O_3};$$

$$\text{ODC: } \underset{100.0}{Al_2O_3} \rightarrow \underset{78.0}{CeO_2} \approx \underset{73.0}{Nd_2O_3} \rightarrow \underset{58.0}{CdO} \approx \underset{56.2}{Y_2O_3} \rightarrow \underset{46.0}{ZnO} \approx \underset{44.0}{CuO} \approx \underset{40.4}{Bi_2O_3} \approx \underset{35.5}{V_2O_5} \rightarrow \underset{7.0}{SnO_2} \approx \underset{5.0}{Sb_2O_3};$$

$$\text{Cr: } \underset{35.4}{CuO} \rightarrow \underset{11.0}{SnO_2} \approx \underset{10.3}{Y_2O_3} \approx \underset{8.0}{Bi_2O_3} \rightarrow \underset{0}{V_2O_5} \approx \underset{0}{CeO_2} \approx \underset{0}{Al_2O_3} \approx \underset{0}{Sb_2O_3} \approx \underset{0}{Nd_2O_3} \approx \underset{0}{CdO} \approx \underset{0}{ZnO}.$$

Obviously, systems containing antimony and tin oxides have the maximum number of transparent coatings. Systems with CeO_2, Y_2O_3, Nd_2O_3, and Bi_2O_3 have less transparent films (21 – 27%), and coatings with cadmium and aluminum oxides altogether have no coatings of good quality.

Zinc, vanadium, and cadmium oxides produce turbidity in films, presumably, due to the processes of microcrystallization or liquation. Aluminum, cerium, and neodymium oxides presumably increase significantly the surface tension of the FFS, as a consequence, the wettability of the glass substrate surface by the solution deteriorates, therefore, the coating fully or partly loses its continuity. Copper oxide significantly intensifies crystallization, accordingly, large dendrite-shaped crystals are formed in films.

TABLE 2

Binary systems (Me_xO_y), containing	Relative number of films, %, of categories			
	T	OC	ODC	Cr
V_2O_5	17.0	47.5	35.5	–
SnO_2	59.0	22.0	7.0	11.0
CeO_2	22.0	–	78.0	–
Al_2O_3	–	–	100.0	–
Y_2O_3	21.0	12.5	56.2	10.3
Sb_2O_3	73.0	22.0	5.0	–
Nd_2O_3	27.0	–	73.0	–
Bi_2O_3	25.6	26.0	40.4	8.0
CuO	2.6	18.0	44.0	35.4
ZnO	4.0	50.0	46.0	–
CdO	–	42.0	58.0	–

Thus, antimony and tin oxides are the most promising for making transparent films. To expand the possibilities and correct the properties of films, the second component can be CeO_2, Y_2O_3, Nd_2O_3, Bi_2O_3, and V_2O_5, since in limited quantities (not more than 20 – 50 mol.%) they do not impair the clarity and continuity of coatings. Zinc, copper, cadmium, and aluminum oxides are not advisable for application, since they do not produce films of optical quality.

Below are refractive indexes of some oxides in glass based on the data from [1].

Oxide	**Refractive index**
SnO_2	1.94
Bi_2O_3	3.15
Sb_2O_3	2.57
Y_2O_3	2.26
ZnO	1.71
CdO	1.805 – 1.925 (mean 1.865)

Evidently, the specified oxides are ranked in the following series in the order of a decreasing refractive index:

$$Bi_2O_3 \rightarrow Sb_2O_3 \rightarrow Y_2O_3 \rightarrow SnO_2 \rightarrow CdO \rightarrow ZnO. \quad (1)$$

It is known [2] that the refractive index of glass is an additive property depending on the refractive indexes of its constituent oxides. Since sol-gel films are amorphous vitreous bodies [3], they have to obey the same law. However, the low thickness and, consequently, the high porosity of clear coatings introduce corrections in the refractive index decrease, according to the following expression [4]:

$$n_{ef} = n_1 - \text{Por}\,(n_1 - n_3) - (n_2 - n_3)\,f\,(P/P_0),$$

where n_1, n_2, and n_3 are the refractive indexes of the skeleton material of the film, adsorbed water, and air, respec-

TABLE 3

Films from FFS with total weight content, %	Distribution of properties in films containing									Parameter distribution interval
	V_2O_5	SnO_2	CeO_2	Nd_2O_3	Bi_2O_3	Sb_2O_3	Y_2O_3	ZnO	CdO	
					Refractive index					
5.0	20	23	–	–	66	–	14	50	67	< 1.6
2.5	14	5	–	–	0	–	14	0	33	
5.0	20	15	0	0	0	15	29	50	33	1.6 – 1.7
2.5	57	50	28	50	40	10	72	0	33	
5.0	40	62	67	33	0	46	43	0	0	1.7 – 1.8
2.5	14	35	29	50	20	50	14	100	33	
5.0	20	0	0	0	0	23	14	–	–	1.8 – 1.9
2.5	14	10	28	–	20	20	0	–	–	
5.0	–	–	33	33	0	15	–	–	–	1.9 – 2.0
2.5	–	–	14	0	20	20	–	–	–	
5.0	–	–	–	33	33	–	–	–	–	> 2.0
2.5	–	–	–	0	0	–	–	–	–	
					Thickness, Å					
5.0	20	15	0	33	–	7	0	0	0	< 300
2.5	42.5	40	14	0	–	30	14	100	33	
5.0	20	32	100	33	0	62	14	50	0	300 – 600
2.5	42.5	35	57	0	67	40	58	–	33	
5.0	40	7	0	33	33	23	14	–	0	600 – 900
2.5	15	20	29	100	33	10	14	–	33	
5.0	–	46	–	–	67	7	58	50	67	900 – 1200
2.5	–	5	–	–	0	20	14	0	0	
5.0	40	–	–	–	–	–	14	–	33	> 1200
2.5	0	–	–	–	–	–	–	–	0	
					Reflection coefficient, %					
5.0	0	–	–	0	–	0	0	–	–	< 10
2.5	17	–	–	50	–	14	20	–	–	
5.0	–	9	0	0	0	9	25	0	0	10 – 15
2.5	–	50	57	50	25	57	20	100	33	
5.0	33	73	20	33	33	36	50	–	100	15 – 20
2.5	50	39	29	0	25	14	75	–	67	
5.0	0	9	40	–	33	0	25	–	–	20 – 25
2.5	33	5.5	14	–	25	14	0	–	–	
5.0	33	9	40	33	0	45	–	–	–	25 – 30
2.5	0	5.5	0	0	25	0	–	–	–	
5.0	33	–	–	33	33	9	–	–	–	> 30
2.5	0	–	–	0	0	0	–	–	–	

tively; $f(P/P_0)$ is the adsorption isotherm equation in the general form; Por is porosity.

As a consequence, the refractive index of films produced from 2.5% FFS is slightly lower than from 5% solutions. This is evident in the data of Table 3 which present the distribution of films by their refractive index, reflection coefficient, and thickness.

The analysis of data in Table 3 established the following:

Film-forming system	**Maximum registered refractive index**
$SnO_2 – Me_xO_y$	1.8 – 1.9
$Bi_2O_3 – Me_xO_y$	> 2.0
$Sb_2O_3 – Me_xO_y$	1.9 – 2.0
$Y_2O_3 – Me_xO_y$	1.8 – 1.9
$ZnO – Me_xO_y$	1.7 – 1.8
$CdO – Me_xO_y$	1.7 – 1.8

Hence one can determine the approximated distribution of binary film-forming system containing the oxides listed below based on their refractive index:

$$Bi_2O_3 \rightarrow Sb_2O_3 \rightarrow SnO_2,\ Y_2O_3 \rightarrow ZnO,\ CdO. \quad (2)$$

Evidently, this series is very close to series (1). Therefore, in developing compositions for highly refractive coatings one should be guided by the values of refractive indexes of the constituent oxides taking into account the porosity-related effects.

A similar analysis for the reflection coefficient yielded the following ranking of systems in the order of a decreasing reflection coefficient:

$$Bi_2O_3,\ Sb_2O_3 \rightarrow SnO_2 \rightarrow Y_2O_3,\ CdO \rightarrow ZnO. \quad (3)$$

In the first approximation, series (1) – (3) are close, i.e., the reflection coefficient of films depends on their refractive index and is related to the refractive indexes of oxides integrating the particular system.

The film thickness regularly grows with an increasing concentration of the FFS applied. It is noted that the thickness of different coatings obtained from FFS with equal concentrations perceptibly grows, as their content of a component with poor film-forming capacity increases. For instance, as the molar content of yttrium oxides grows from 20 to 80% in the $SnO_2 - Y_2O_3$ system, the film thickness grows 2.5 times (the films are produced from 2.5% FFS) and in the system $Sb_2O_3 - Y_2O_3$ it grows 2.8 times (the films are obtained from 5% solutions). This does not occur in the $Sb_2O_3 - SnO_2$ system where both oxides have good film-forming capacities.

Thus, antimony and tin oxides are the most promising for producing clear films. To expand the possibilities and correct film properties, the second component can be CeO_2, Y_2O_3, Nd_2O_3, Bi_2O_3, or V_2O_5, which for the molar ration of 20 – 50% do not impair the clarity and continuity of coatings. Zinc, copper, cadmium, and aluminum oxides are not advisable for application, since they do not produce films of optical quality.

REFERENCES

1. A. A. Appen, *Chemistry of Glass* [in Russian], Khimiya, Leningrad (1972).
2. *Physicochemical Principles of Production of Optical Glass* [in Russian], Khimiya, Leningrad (1976).
3. N. V. Suikovskaya, *Chemical Methods of Producing Thin Clear Films* [in Russian], Khimiya, Leningrad (1971).
4. P. G. Cheremskoi, V. V. Slezov, and V. I. Betekhtin, *Pores in a Solid Body* [in Russian], Énergoatomizdat, Moscow (1990).